Provide Thermogravimetric Analysis Data to Performance Assessment

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Recent experimental testing has investigated the effect of a deposited "mixed" salt on the corrosion of carbon steel in high relative humidity air. This result is compared with previous studies where pure sodium chloride was deposited. There are aspects of the degradation process which are significantly different when the different salts are deposited. With deposited sodium chloride, corrosion occurs almost immediately after introduction of 80% RH air. With deposited "mixed" salts, there is an initial inhibition of corrosion in 80% RH air. After the initial inhibition period, corrosion occurs at "localized" regions of the specimen. At longer times, the specimen suffers extensive corrosion. A very porous and non-adherent corrosion product forms and readily spalls.

The initial inhibition of the corrosion with the deposited "mixed" salt is most likely due to the bicarbonate component. Bicarbonate is a known inhibitor of general corrosion of carbon steel [Thomas, 1994] and a promoter of localized corrosion at moderate alkalinity when chloride ions are present [Marsh, 1985]. The results of this testing indicate that the bicarbonate component of thin water layers can initially inhibit corrosion of the carbon steel. With time, however, inhibition is lost. A mechanism for this loss of inhibition is suggested.

It is plausible that moderately alkaline bicarbonate aqueous solutions could develop on the surface of a waste package due to "Yucca Mountain water" contacting the waste packages. Aqueous conditions might develop where carbon steel is susceptible to localized corrosion [Dunn, 1998]. The initial test results presented here suggest that the inhibition of general corrosion, and hence, the promotion of localized corrosion of carbon steel by thin aqueous bicarbonate-chloride layers may not be sustainable. Additional testing is underway to further understand the effects of thin aqueous solution chemistry on carbon steel corrosion.
The carbon steel specimen was made of ASTM A516 Gr 55 and had dimensions of 5.10 cm x 1.24 cm x 0.156 cm. The "mixed" salt was deposited on the carbon steel specimen from an aerosol which was produced by a nebulizer. Visual inspection indicates that the salts are deposited more or less uniformly across the surface. The amount of salt that was deposited was about 7.5 mg. The aqueous solution, which fed the nebulizer, was made to give the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>12330</td>
</tr>
<tr>
<td>K</td>
<td>1010</td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
</tr>
<tr>
<td>Cl</td>
<td>2020</td>
</tr>
<tr>
<td>SO4</td>
<td>5010</td>
</tr>
<tr>
<td>NO3</td>
<td>1920</td>
</tr>
<tr>
<td>F</td>
<td>430</td>
</tr>
<tr>
<td>HCO3</td>
<td>21360</td>
</tr>
<tr>
<td>Si</td>
<td>28</td>
</tr>
</tbody>
</table>

The actual composition of the salt deposited has not yet been determined.

The specimen was vertically oriented in a reaction chamber, which is double-walled glass cylinder. Heat was supplied to the chamber by flowing a transparent oil at a constant temperature through the outer annulus of the chamber. The glass reaction chamber allowed the monitoring of the specimen's surface during the testing. Temperature and relative humidity in the reaction chamber were continuously monitored and controlled. The variation in relative humidity was ±2%. A thermogravimetric analyzer was used to monitor the weight change of specimen with time.
The results for testing with deposited sodium chloride and with deposited “mixed” salts are shown in Figure 1. The test temperature was 77°C and the nominal relative humidity was 80%.

With deposited sodium chloride, the visible appearance of corrosion product occurred within a half hour of reaching the reaction conditions. The weight of the specimen started to increase even before reaching the test conditions. Some of this weight gain is probably due to water sorption by the hygroscopic salt, but the rapid appearance of the corrosion product indicates that a portion of the initial weight gain is due to oxidation/corrosion of the specimen. The corrosion product formed more or less uniformly across the surface. At no time was the visible appearance of sorbed water noted.

For the next 250 hrs, the weight gain of the specimen increased. It was noted by visual inspection that the amount of corrosion product was increasing concomitantly. After approximately 250 hrs, the rate of weight gain decreased significantly. It was also noted that spalling of corrosion product off of the vertically oriented specimen was occurring at this time. In Figure 1, spalling is marked by the steep drops in the weight of the specimen. It should be noted that there was usually an increase in the weight gain of the specimen after the corrosion product spalling. Again, at no time was the visible appearance of sorbed water noted.

With deposited “mixed” salts, there was an immediate and steady increase in the weight of the specimen up to about 13.5 mg at test time of 14 hrs. At that time, the weight change of the specimen temporarily ceased. During this time period there was very little visible corrosion product (one small spot) on the surface of the specimen. The surface glistened with water sorbed by the salts. A significant amount of water also accumulated at the bottom of the vertically oriented test specimen.
With continued exposure, the appearance of corrosion product was noted. In contrast to the deposited sodium chloride salt, the corrosion started at isolated portions of the specimen and grew from these initiation points. At one part of the specimen the corrosion grew radially out and eventually covered a significant portion of the specimen. At other areas of the surface, the corrosion product was isolated at numerous spots of small diameters. With time the diameters of some of the corrosion spots grew and coalesced.

The corrosion product that formed on the surface with the deposited “mixed” salts was porous, non-adherent, and readily spalled. Visual inspection noted that the corrosion product spalled at much earlier times than that with deposited sodium chloride. That the corrosion product spalled is also apparent from the fact that the overall weight change became negative after about 280 hrs of testing.

The initial inhibition of the carbon steel corrosion when the “mixed” salts are deposited might be attributable to the bicarbonate component of the salt. The initial loss of this inhibition must be due to local variation in aqueous film composition. A concentration of aggressive ions such as chloride, or a decrease in the inhibiting ion such as bicarbonate are both possible. A plausible mechanism for the loss of this inhibition due to a decrease in bicarbonate ions is now given.

In the corrosion of carbon steel, iron is oxidized to the Fe(+2) state, that is:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- . \]

The iron ions will hydrolyze, which results in hydrogen ions being formed:

\[ \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ . \]

With sufficient bicarbonate or hydroxyl ions present the hydrogen ions will be consumed:

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \text{or} \]

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]
At some point the limited amount of hydroxyl / bicarbonate ions in the thin aqueous film is consumed. This results in a local acidification and facilitates further corrosion using reduction of hydrogen as the cathodic reaction. The bicarbonate is continually consumed, the aqueous solution pH decreases, and corrosion spreads across the surface.

This is in contrast to the bulk aqueous solution testing that was conducted by Marsh [Marsh, 1985]. In bulk solutions there is a large reservoir from which the bicarbonate that is consumed can be resupplied.

The present results are consistent with the bicarbonate ion in the thin aqueous solutions providing the initial inhibition, and the “consumption” of the bicarbonate resulting in breakdown of the inhibition. Testing is in progress or planned to further investigate the initial inhibition and the subsequent breakdown of the inhibition.

References


Material: A516 Gr55 (carbon steel)
Temperature: 77°C
Nominal Relative Humidity: 80%

With deposited Sodium Chloride (NaCl)
With deposited "mixed" salt